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(71) Applicant: BP Chemicals Limited  
London EC2M 7BA (GB)

(72) Inventors:  
• Baker, Michael James, Res. Centre Warrensville  
Ohio 44128-2837 (US)

- Giles, Martin Francis, BP Chemicals Ltd.  
London, EC2M 7BA (GB)
- Garland, Carl Sherman  
Silver Spring, Maryland 20901 (US)
- Rafeletos, Georgios  
Canterbury, Kent CT2 7SR (GB)

(74) Representative: Perkins, Nicholas David et al  
BP International Limited  
Patents and Agreements Division,  
Chertsey Road  
Sunbury-on-Thames, Middlesex TW16 7LN (GB)

(54) Process for the carbonylation of alkyl alcohols and/or reactive derivatives thereof

(57) In a process for the liquid phase carbonylation of an alkyl alcohol such as methanol, and/or a reactive derivative thereof to produce the corresponding carboxylic acid and/or ester, in the presence of an iridium cat-

alyst, an alkyl halide and water, the reaction is promoted by the presence of at least one promoter selected from cadmium, mercury, zinc, gallium, indium and tungsten, optionally with a co-promoter selected from ruthenium, osmium and rhenium.

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## Description

The present invention relates to a carbonylation process and in particular to a process for the carbonylation of alkyl alcohols and/or reactive derivatives thereof in the presence of an iridium catalyst.

Carbonylation processes in the presence of iridium catalysts are known and are described, for example, in US 3772380, European patent publication number EP 0618184-A, UK patents GB 1276326, GB 1234641 and GB 1234642.

Carbonylation in the presence of an iridium catalyst and co-promoter selected from ruthenium and osmium is described in European patent publication number EP-0643034-A.

It has now been found that a promoter selected from the group consisting of cadmium, mercury, zinc, gallium, indium and tungsten has a beneficial effect on the rate of carbonylation of an alkyl alcohol and/or a reactive derivative thereof in the presence of an iridium catalyst.

Thus, according to the present invention there is provided a process for the production of a carboxylic acid by carbonylation of an alkyl alcohol and/or a reactive derivative thereof which process comprises contacting in a carbonylation reactor said alcohol and/or a reactive derivative thereof with carbon monoxide in a liquid reaction composition comprising: (a) an iridium catalyst, (b) an alkyl halide, (c) at least a finite concentration of water, and (d) a promoter selected from the group consisting of cadmium, mercury, zinc, gallium, indium and tungsten.

Also according to the present invention there is provided a catalyst system for the carbonylation of an alkyl alcohol and/or a reactive derivative thereof which catalyst system comprises (a) an iridium catalyst, (b) an alkyl halide and (c) a promoter selected from the group consisting of cadmium, mercury, zinc, gallium, indium and tungsten.

The promoters of the present invention are not only generally cheaper than promoters such as ruthenium and osmium, but at least cadmium, mercury, zinc, gallium and indium are believed to be less likely to form volatile species in the carbonylation reaction.

Suitable alkyl alcohols comprise  $C_1$  to  $C_{10}$ , preferably  $C_1$  to  $C_6$ , more preferably  $C_1$  to  $C_4$  alkyl alcohols and yet more preferably methanol. Preferably, the alkyl alcohol is a primary or secondary alkyl alcohol. The product of the carbonylation of an alcohol having  $n$  carbon atoms and/or a derivative thereof is a carboxylic acid having  $n+1$  carbon atoms and/or an ester of a carboxylic acid having  $n+1$  carbon atoms and the alcohol having  $n$  carbon atoms. Thus the product of the carbonylation of methanol and/or a derivative thereof is acetic acid and/or methyl acetate.

Suitable reactive derivatives of the alkyl alcohol include the corresponding alkyl ester of the alcohol and the corresponding carboxylic acid product, dialkyl ethers and alkyl halides, preferably iodides or bromides. Suitable reactive derivatives of methanol include methyl acetate, dimethyl ether and methyl iodide. A mixture of alkyl alcohol and reactive derivatives thereof may be used as reactants in the process of the present invention. Preferably, methanol and/or methyl acetate are used as reactants. At least some of the alkyl alcohol and/or reactive derivative thereof will be converted to, and hence present as, alkyl esters in the liquid reaction composition by reaction with carboxylic acid product or solvent. The concentration in the liquid reaction composition, of alkyl ester is suitably in the range 1 to 70% by weight, preferably 2 to 50% by weight and yet more preferably 3 to 35% by weight.

Water may be formed in situ in the liquid reaction composition, for example, by the esterification reaction between alkyl alcohol reactant and carboxylic acid product. Water may be introduced to the carbonylation reactor together with or separately from other components of the liquid reaction composition. Water may be separated from other components of reaction composition withdrawn from the reactor and may be recycled in controlled amounts to maintain the required concentration of water in the liquid reaction composition. Suitably, the concentration of water in the liquid reaction composition is in the range 1 to 15% by weight, preferably 1 to 10% by weight, more preferably no greater than 6.5% by weight.

The iridium component of the catalyst in the liquid reaction composition may comprise any iridium containing compound which is soluble in the liquid reaction composition. The iridium component of the catalyst may be added to the liquid reaction composition for the carbonylation reaction in any suitable form which dissolves in the liquid reaction composition or is convertible to a soluble form. Examples of suitable iridium-containing compounds which may be added to the liquid reaction composition include  $IrCl_3$ ,  $IrI_3$ ,  $IrBr_3$ ,  $[Ir(CO)_2I]_2$ ,  $[Ir(CO)_2Cl]_2$ ,  $[Ir(CO)_2Br]_2$ ,  $[Ir(CO)_2I_2] \cdot H^+$ ,  $[Ir(CO)_2Br_2] \cdot H^+$ ,  $[Ir(CO)_2I_2] \cdot H^+$ ,  $[Ir(CH_3)_3(CO)_2] \cdot H^+$ ,  $Ir_4(CO)_{12}$ ,  $IrCl_3 \cdot 3H_2O$ ,  $IrBr_3 \cdot 3H_2O$ ,  $Ir_4(CO)_{12}$ , iridium metal,  $Ir_2O_3$ ,  $IrO_2$ ,  $Ir(acac)(CO)_2$ ,  $Ir(acac)_3$ , iridium acetate,  $[Ir_3O(OAc)_6(H_2O)_3][OAc]$ , and hexachloroiridic acid  $[H_2IrCl_6]$ , preferably, chloride-free complexes of iridium such as acetates, oxalates and acetoacetates which are soluble in one or more of the carbonylation reaction components such as water, alcohol and/or carboxylic acid. Particularly preferred is green iridium acetate which may be used in an acetic acid or aqueous acetic acid solution.

Preferably, the iridium catalyst concentration in the liquid reaction composition is in the range 100 to 6000 ppm by weight of iridium.

The cadmium, mercury, zinc, gallium, indium or tungsten promoter may comprise any cadmium, mercury, zinc, gallium, indium or tungsten containing compound which is soluble in the liquid reaction composition. The promoter may be added to the liquid reaction composition for the carbonylation reaction in any suitable form which dissolves in the liquid reaction composition or is convertible to a soluble form.

Examples of suitable cadmium-containing compounds which may be used include  $\text{Cd}(\text{OAc})_2$ ,  $\text{CdI}_2$ ,  $\text{CdBr}_2$ ,  $\text{CdCl}_2$ ,  $\text{Cd}(\text{OH})_2$ , and cadmium acetylacetonate.

Examples of suitable mercury-containing compounds which may be used include  $\text{Hg}(\text{OAc})_2$ ,  $\text{HgI}_2$ ,  $\text{HgBr}_2$ ,  $\text{HgCl}_2$ ,  $\text{Hg}_2\text{I}_2$ , and  $\text{Hg}_2\text{Cl}_2$ .

Examples of suitable zinc-containing compounds which may be used include  $\text{Zn}(\text{OAc})_2$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{ZnI}_2$ ,  $\text{ZnBr}_2$ ,  $\text{ZnCl}_2$ , and zinc acetylacetonate.

Examples of suitable gallium-containing compounds which may be used include gallium acetylacetonate, gallium acetate,  $\text{GaCl}_3$ ,  $\text{GaBr}_3$ ,  $\text{GaI}_3$ ,  $\text{Ga}_2\text{Cl}_4$  and  $\text{Ga}(\text{OH})_3$ .

Examples of suitable indium-containing compounds which may be used include indium acetylacetonate, indium acetate,  $\text{InCl}_3$ ,  $\text{InBr}_3$ ,  $\text{InI}_3$ ,  $\text{InI}$  and  $\text{In}(\text{OH})_3$ .

Examples of suitable tungsten-containing compounds which may be used include  $\text{W}(\text{CO})_6$ ,  $\text{WCl}_4$ ,  $\text{WCl}_6$ ,  $\text{WBBr}_5$ ,  $\text{WI}_2$ ,  $\text{C}_9\text{H}_{12}\text{W}(\text{CO})_3$  and any tungsten chloro-, bromo- or iodo-carbonyl compound.

The molar ratio of each promoter : iridium catalyst is suitably in the range (0.1 to 20):1, preferably (0.5 to 10):1. More than one promoter may be used.

An optional co-promoter selected from the group consisting of ruthenium, osmium and rhenium may also be used and may comprise any ruthenium, osmium or rhenium containing compound which is soluble in the liquid reaction composition. The optional co-promoter may be added to the liquid reaction composition for the carbonylation reaction in any suitable form which dissolves in the liquid reaction composition or is convertible to a soluble form.

Examples of suitable ruthenium-containing compounds which may be used as optional co-promoter include ruthenium (III) chloride, ruthenium (III) chloride trihydrate, ruthenium (IV) chloride, ruthenium (III) bromide, ruthenium metal, ruthenium oxides, ruthenium (III) formate,  $[\text{Ru}(\text{CO})_3\text{I}_3]\text{H}^+$ ,  $[\text{Ru}(\text{CO})_2\text{I}_2]_n$ ,  $[\text{Ru}(\text{CO})_4\text{I}_2]$ ,  $[\text{Ru}(\text{CO})_3\text{I}_2]_2$ , tetra(aceto)chlororuthenium(II,III), ruthenium (III) acetate, ruthenium (III) propionate, ruthenium (III) butyrate, ruthenium pentacarbonyl, trirutheniumdodecacarbonyl and mixed ruthenium halocarbonyls such as dichlorotricarbonylruthenium (II) dimer, dibromotricarbonylruthenium (II) dimer, and other organoruthenium complexes such as tetrachlorobis(4-cymene)diruthenium(II), tetrachlorobis(benzene)diruthenium(II), dichloro(cycloocta-1,5-diene)ruthenium (II) polymer and tris(acetylacetonate)ruthenium (III).

Examples of suitable osmium containing compounds which may be used as optional co-promoter include osmium (III) chloride hydrate and anhydrous, osmium metal, osmium tetraoxide, triosmiumdodecacarbonyl,  $[\text{Os}(\text{CO})_4\text{I}_2]$ ,  $[\text{Os}(\text{CO})_3\text{I}_2]_2$ ,  $[\text{Os}(\text{CO})_3\text{I}_3]\text{H}^+$ , pentachloro- $\mu$ -nitrodiosmium and mixed osmium halocarbonyls such as tricarbonyldichlorooosmium (II) dimer and other organoosmium complexes.

Examples of suitable rhenium-containing compounds which may be used as optional co-promoter include  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{Re}(\text{CO})_5\text{Cl}$ ,  $\text{Re}(\text{CO})_5\text{Br}$ ,  $\text{Re}(\text{CO})_5\text{I}$ ,  $\text{ReCl}_3 \cdot x\text{H}_2\text{O}$ ,  $[\text{Re}(\text{CO})_4\text{I}]_2$ ,  $[\text{Re}(\text{CO})_4\text{I}_2]\text{H}^+$  and  $\text{ReCl}_5 \cdot y\text{H}_2\text{O}$ .

The molar ratio of each optional co-promoter : iridium catalyst is suitably in the range (0.1 to 20):1, preferably (0.5 to 10):1.

Preferably, the iridium, promoter and optional co-promoter containing compounds are free of impurities which provide or generate in situ ionic iodides which may inhibit the reaction, for example, alkali or alkaline earth metal or other metal salts.

Ionic contaminants such as, for example, (a) corrosion metals, particularly nickel, iron and chromium and (b) phosphines or nitrogen containing compounds or ligands which may quaternise in situ: should be kept to a minimum in the liquid reaction composition as these will have an adverse effect on the reaction by generating  $\text{I}^-$  in the liquid reaction composition which has an adverse effect on the reaction rate. Some corrosion metal contaminants such as for example molybdenum have been found to be less susceptible to the generation of  $\text{I}^-$ . Corrosion metals which have an adverse affect on the reaction rate may be minimised by using suitable corrosion resistant materials of construction. Similarly, contaminants such as alkali metal iodides, for example lithium iodide, should be kept to a minimum. Corrosion metal and other ionic impurities may be reduced by the use of a suitable ion exchange resin bed to treat the reaction composition, or preferably a catalyst recycle stream. Such a corrosion metal removal process is described in US 4007130. Preferably, ionic contaminants are kept below a concentration at which they would generate 500 ppm  $\text{I}^-$ , preferably less than 250 ppm  $\text{I}^-$  in the liquid reaction composition.

Suitable alkyl halides have alkyl moieties corresponding to the alkyl moiety of the alkyl alcohol reactant and are preferably  $\text{C}_1$  to  $\text{C}_{16}$ , more preferably  $\text{C}_1$  to  $\text{C}_6$  and yet more preferably  $\text{C}_1$  to  $\text{C}_4$  alkyl halides. Preferably the alkyl halide is an iodide or bromide, more preferably an iodide. A preferred alkyl halide is methyl iodide. Preferably, the concentration of alkyl halide in the liquid reaction composition is in the range 1 to 20%, preferably 2 to 16% by weight.

The carbon monoxide reactant may be essentially pure or may contain inert impurities such as carbon dioxide, methane, nitrogen, noble gases, water and  $\text{C}_1$  to  $\text{C}_4$  paraffinic hydrocarbons. The presence of hydrogen in the carbon monoxide and generated in situ by the water gas shift reaction is preferably kept low, for example, less than 1 bar partial pressure, as its presence may result in the formation of hydrogenation products. The partial pressure of carbon monoxide in the reaction is suitably in the range 1 to 70 bar, preferably 1 to 35 bar, more preferably 1 to 15 bar.

The total pressure of the carbonylation reaction is suitably in the range 10 to 200 barg, preferably 10 to 100 barg.

more preferably 15 to 50 barg. The temperature of the carbonylation reaction is suitably in the range 100 to 300 °C, preferably in the range 150 to 220 °C

Carboxylic acid and/or ester thereof may be used as a solvent for the reaction.

The process of the present invention may be performed as a batch or a continuous process, preferably as a continuous process.

The carboxylic acid and/or ester thereof product may be removed from the reactor by withdrawing liquid reaction composition and separating the carboxylic acid product and/or ester thereof by one or more flash and/or fractional distillation stages from the other components of the liquid reaction composition such as iridium catalyst, cadmium, mercury, zinc, gallium, indium or tungsten promoter, optional co-promoter, alkyl halide, water and unconsumed reactants which may be recycled to the reactor to maintain their concentrations in the liquid reaction composition. The carboxylic acid product and/or ester thereof may also be removed as a vapour from the reactor.

The invention will now be illustrated by way of example only by reference to the following examples.

#### Cadmium, mercury and zinc promoters

A 150 cm<sup>3</sup> Hastelloy B2 (Trade Mark) autoclave equipped with a Magnedrive (Trade Mark) stirrer, liquid injection facility and cooling coils was used for a series of batch carbonylation experiments. A gas supply to the autoclave was provided from a ballast vessel, feed gas being provided to maintain the autoclave at a constant pressure. The rate of gas uptake at a certain point in a experiment was used to calculate the carbonylation rate, as number of moles of reactant consumed per litre of cold degassed reactor composition per hour (mol/l/hr), at a particular reactor composition (reactor composition based on a cold degassed volume).

The methyl acetate concentration was calculated during the course of the reaction from the starting composition, assuming that one mole of methyl acetate is consumed for every mole of carbon monoxide that is consumed. No allowance was made for organic components in the autoclave headspace. The data are reported at calculated methyl acetate concentrations of 26%, 15% and 6% which correspond to typical standing concentrations in the liquid reaction composition in a continuous process. For 15% calculated methyl acetate concentration in such a continuous process the concentration of other components of such a liquid reaction composition are: methyl iodide about 5 to 8%, typically about 5 to 6%, water about 6 to 8% and acetic acid balance.

For each batch carbonylation experiment the autoclave was charged with cadmium, mercury or zinc promoter, optional co-promoter and the liquid components of the liquid reaction composition excluding part of the water charge (6.5 g), in which the iridium catalyst was dissolved (see Table 1).

The autoclave was flushed twice with nitrogen and once with carbon monoxide (being pressurised with each gas to approximately 25 barg) and was then heated, by means of electrical heating coils, to a temperature of 190°C under 1 bara pressure of carbon monoxide. A rapid and consistent rate of stirring (1000 rpm) was employed. Once stable at temperature the aqueous iridium catalyst solution was injected into the autoclave. Simultaneously, the autoclave was pressurised to 22 barg with carbon monoxide fed from the ballast vessel. The pressure in the autoclave was subsequently maintained at approximately 22 barg (see Table 2) with carbon monoxide fed from the ballast vessel. The partial pressure of carbon monoxide was not measured but was believed to be less than 15 bar. The reaction temperature was maintained within  $\pm 1$  °C of the desired reaction temperature (190 °C).

Gas uptake from the ballast vessel was measured throughout the course of the experiment and used to calculate carbonylation rate. After uptake of carbon monoxide from the ballast vessel has ceased the autoclave was isolated from the gas supply and was cooled to room temperature by means of the cooling coils. The autoclave was vented and samples of the liquid reaction composition and gases in the headspace of the autoclave were analysed by gas chromatography. The major product in each batch carbonylation experiment according to the present invention was acetic acid. By-product yields are collated in Table 2.

#### Examples 1-10 and Experiments A-I

The results given in Table 2 show that cadmium does not act as a carbonylation catalyst under the reaction conditions (Experiment D). The results in Table 2 also show that cadmium promotes iridium catalysed methanol carbonylation (compare Examples 1-3 with Experiments A-D). The results in Table 2 show that the carbonylation rate increases as the cadmium concentration increases. The results in Table 2 show that mercury and zinc are also promoters for iridium catalysed carbonylation of methanol (Examples 4-7), but are not as effective as cadmium.

The results in Table 2 also show that cadmium and zinc promote an iridium/ruthenium carbonylation of methanol (Experiment E compared with Examples 8, 9 and 10).

No evidence of precipitation was observed in Examples 1 to 7 which indicates that cadmium, mercury and zinc are soluble

Table 1 Autoclave Charges

Experiment	Catalyst System (molar ratio)	Catalyst $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (g)	Optional Co-Promoter $\text{Ru}_3(\text{CO})_{12}$ (g)	Promoter	Amount of Promoter (g)	Methyl Acetate (g)	Water (g)	Methyl iodide (g)	Acetic Acid (g)
Experiment A	Ir	0.331	-	-	-	28.80	10.20	5.35	45.34
Experiment B	Ir	0.331	-	-	-	28.80	10.15	5.31	45.32
Experiment C	Ir	0.331	-	-	-	28.80	10.17	6.67	44.00
Experiment D	Cd (2)	-	-	$\text{CdI}_2$	0.680	28.80	10.24	4.81	45.46
Example 1	Ir/Cd (1:2)	0.331	-	$\text{CdI}_2$	0.680	28.81	10.20	5.34	44.66
Example 2	Ir/Cd (1:5)	0.331	-	$\text{CdI}_2$	1.710	28.80	10.17	5.33	43.68
Example 3	Ir/Cd (1:10)	0.331	-	$\text{CdI}_2$	3.430	28.80	10.18	5.44	41.92
Example 4	Ir/Hg (1:5)	0.331	-	$\text{HgI}_2$	2.130	28.80	10.16	5.33	43.21
Example 5	Ir/Hg (1:5)	0.331	-	$\text{Hg}(\text{OAc})_2$	1.490	28.80	10.18	6.65	42.57
Example 6	Ir/Zn (1:5)	0.331	-	$\text{ZnI}_2$	1.490	28.80	10.16	5.35	43.84
Example 7	Ir/Zn (1:5)	0.331	-	$\text{ZnCl}_2$	0.633	28.81	10.17	6.65	43.36
Experiment E	Ir/Ru (1:2)	0.332	0.401	-	-	28.81	10.18	5.87	44.42
Experiment F	Ir/Ru (1:5)	0.331	0.995	-	-	28.81	10.17	6.70	43.04
Experiment G	Ir/Re (1:5)	0.331	1.535g $\text{Re}_2(\text{CO})_{10}$	-	-	28.80	10.16	7.31	41.85
Experiment H	Ir/Ru/Os (1:2:2)	0.331	0.401 and 0.568g $\text{Os}_3(\text{CO})_{12}$	-	-	28.82	10.18	6.38	43.31
Experiment I	Ir/Ru/Re (1:2:2)	0.332	0.400 and 0.613g $\text{Re}_2(\text{CO})_{10}$	-	-	28.80	10.19	6.69	43.00
Example 8	Ir/Ru/Cd (1:2:2)	0.331	0.400	$\text{CdI}_2$	0.679	28.80	10.17	5.83	43.75
Example 9	Ir/Ru/Cd (1:2:2)	0.332	0.401	$\text{CdI}_2$	0.682	28.82	10.17	5.86	43.73
Example 10	Ir/Ru/Zn (1:2:2)	0.331	0.401	$\text{ZnCl}_2$	0.256	28.81	10.17	6.39	43.63

Table 2 Rate, Stability and By-product Data

Run	Reactor Pressure at 15 wt% Methyl acetate <sup>c</sup>	Rate at 26, 15 and 6% wt% MeOAc concentration <sup>c</sup> (Mol/l/hr)	[Ethyl Iodide] (ppm)	[Ethyl Acetate] (ppm)	[Propionic Acid] (ppm)	Methane <sup>a</sup>	Carbon Dioxide <sup>a</sup>	Appearance of Reaction Composition at End of Experiment
Experiment A	22.4	11.1 9.0 4.2	456	233	84	12.5	11.3	Orange solution
Experiment B	22.6	9.9 8.1 3.8	201	216	141	10.7	5.8	Orange solution
Experiment C	22.8	9.9 8.3 4.4						Orange solution
Experiment D	(23.7) <sup>b</sup>	0.0	<2	65	55	2.0	0.9	Off-white solution
Example 1	22.6	14.5 13.3 7.5	661	306	115	15.5	9.9	Orange solution
Example 2	22.6	18.4 16.3 11.3	653	236	118	17.0	20.4	Orange solution
Example 3	22.5	19.2 17.6 11.9	626	155	122	16.7	35.5	Brown-green solution
Example 4	22.6	13.7 12.4 5.7	495	232	115	33.7	37.8	Orange solution
Example 5	22.8	13.1 11.8 6.2	305	237	120	38.0	38.7	Orange solution
Example 6	22.8	12.2 11.2 6.1	538	302	146	18.7	10.9	Orange solution
Example 7	22.9	11.1 10.5 5.6	369	289	103	17.4	8.5	Dark orange-brown solution

Table 2 continued Rate, Stability and By-product Data

Run	Reactor Pressure at 15 wt% Methyl acetate <sup>c</sup>	Rate at 26, 15 and 6% wt% MeOAc concentration <sup>c</sup> (Mol/l/hr)	[Ethyl Iodide] (ppm)	[Ethyl Acetate] (ppm)	[Propionic Acid] (ppm)	Methane <sup>a</sup>	Carbon Dioxide <sup>a</sup>	Appearance of Reaction Composition at End of Experiment
Experiment E	22.3	15.1 13.9 9.8	389	211	69	11.2	3.3	Orange solution
Experiment F	22.5	19.1 17.4 11.9	483	149	115	15.3	5.8	Orange precipitate in orange solution
Experiment G	22.8	13.2 11.0 4.7	373	219	109	11.8	6.7	Orange solution
Experiment H	22.9	19.2 18.1 13.0	464	224	75	14.6	9.4	
Experiment I	22.8	17.4 16.3 9.4	482	198	75	11.6	3.8	
Example 8	22.5	18.1 16.5 11.6	696	248	116	15.3	7.4	Orange solution + cloudy orange precipitate
Example 9	22.7	18.7 17.0 11.1	696	246	118	16.0	7.0	Orange solution + cloudy orange precipitate
Example 10	22.9	16.2 15.5 10.7	590	233	114	12.9	6.4	

<sup>a</sup> % by volume of the measured gases (CO, CH<sub>4</sub> and CO<sub>2</sub>); the balance being carbon monoxide

<sup>b</sup> No carbonylation occurred - reactor pressure was therefore not measured at 15 wt% methyl acetate concentration

<sup>c</sup> Calculated concentration of methyl acetate 26%, 15% and 6% by weight-corresponding water concentrations 9.7%, 7.0% and 4.6% respectively. Methyl iodide about 5 to 8%, typically about 5 to 6%. Rate error estimated at  $\pm 10\%$ .  
MeOAc = methyl acetate

Gallium and iridium promoters. Examples 11-14

The same procedure and apparatus as for the cadmium, mercury and zinc promoters was followed. The autoclave charges are given in Table 3 and the results in Table 4 for Examples 11-14. The major product in each batch carbonylation experiment according to the present invention was acetic acid.

The results given in Table 4 show that gallium and indium both promote iridium catalysed methanol carbonylation (compare Examples 11-12 with Experiments A-C).

The results in Table 4 also show that gallium and indium promote iridium/ruthenium carbonylation of methanol; (Experiment E compared with Examples 13-14).

No evidence of precipitation was observed in Examples 11 and 12 which indicates that gallium and indium are soluble.



Table 3 Autoclave Charges

Experiment	Catalyst System (molar ratio)	Catalyst $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (g)	Optional Co-Promoter $\text{Ru}_3(\text{CO})_{12}$ (g)	Promoter	Amount of Promoter (g)	Methyl Acetate (g)	Water (g)	Methyl iodide (g)	Acetic Acid (g)
Experiment A	Ir	0.331	-	-	-	28.80	10.20	5.35	45.34
Experiment B	Ir	0.331	-	-	-	28.80	10.15	5.31	45.32
Experiment C	Ir	0.331	-	-	-	28.80	10.17	6.67	44.00
Example 11	Ir/Ga (1:5)	0.330	-	$\text{GaI}_3$	2.105	28.80	10.17	5.33	43.23
Example 12	Ir/In (1:5)	0.331	-	$\text{InI}_3$	2.305	28.80	10.18	5.38	43.02
Experiment E	Ir/Ru (1:2)	0.332	0.401	-	-	28.81	10.18	5.87	44.42
Example 13	Ir/Ru/Ga (1:2:2)	0.331	0.400	$\text{GaI}_3$	0.848	28.81	10.16	5.85	43.59
Example 14	Ir/Ru/In (1:2:2)	0.331	0.400	$\text{InI}_3$	0.926	28.82	10.17	5.88	43.49

Table 4 Rate, Stability and By-product Data

Experiment	Reactor Pressure at 15 wt% MeOAc concentration <sup>b</sup>	Rate at 26, 15 and 6% wt% MeOAc concentration <sup>b</sup> (Mol/l/hr)	Liquid by-products			Gaseous by-products		Appearance of Reaction Composition at End of Experiment
			[Ethyl Iodide] (ppm)	[Ethyl Acetate] (ppm)	[Propionic Acid] (ppm)	Methane <sup>a</sup>	Carbon Dioxide <sup>a</sup>	
Experiment A	22.4	11.1 9.0 4.2	456	233	84	12.5	11.3	Orange solution
Experiment B	22.6	9.9 8.1 3.8	201	216	141	10.7	5.8	Orange solution
Experiment C	22.8	9.9 8.3 4.4	-	-	-	-	-	Orange solution
Example 11	22.6	13.4 11.3 5.7	497	255	143	17.3	19.3	Orange solution
Example 12	22.8	16.5 13.9 8.0	812	316	153	18.9	24.5	Orange solution
Experiment E	22.3	15.1 13.9 9.8	389	211	69	11.2	3.3	Orange solution
Example 13	22.5	19.7 16.6 9.4	547	161	144	12.0	7.4	Orange solution
Example 14	22.4	19.1 17.3 12.7	682	179	115	12.7	6.1	Orange solution with cloudy suspension

<sup>a</sup> % by volume of the measured gases (CO, CH<sub>4</sub> and CO<sub>2</sub>); the balance being carbon monoxide

<sup>b</sup> Calculated concentration of methyl acetate at 26%, 15% and 6% by weight, corresponding water concentrations 9.7%, 7% and 4.6% respectively. Methyl iodide about 5 to 8%, typically about 5 to 6%. Rate error estimated  $\pm 10\%$ .

MeOAc = methyl acetate.

Tungsten promoter

A 300 cm<sup>3</sup> Hastelloy B2 (Trade Mark) autoclave equipped with a Dispersimax (Trade Mark) stirrer, liquid injection facility and cooling coils was used for a series of batch carbonylation experiments. A gas supply to the autoclave was provided from a ballast vessel, feed gas being provided to maintain the autoclave at a constant pressure. The rate of gas uptake at a certain point in a experiment was used to calculate the carbonylation rate, as number of moles of reactant consumed per litre of cold degassed reactor composition per hour (mol/l/hr), at a particular reactor composition (reactor composition based on a cold degassed volume).

The methyl acetate concentration was calculated during the course of the reaction from the starting composition, assuming that one mole of methyl acetate is consumed for every mole of carbon monoxide that is consumed. No allowance was made for organic components in the autoclave headspace. The data are reported at a calculated methyl acetate concentration of 26, 15 and 6% which corresponds to a typical standing concentration in the liquid reaction composition in a continuous process. For a calculated concentration of methyl acetate of 15% the concentration of other components of such a liquid reaction composition are: methyl iodide about 5 to 8%, typically about 5 to 6%, water about 6 to 8% and acetic acid balance.

For each batch carbonylation experiment the autoclave was charged with tungsten promoter, optional co-promoter and the liquid components of the liquid reaction composition excluding part of the water charge (10.83 g), in which the iridium catalyst was dissolved (see Table 5).

The autoclave was flushed once with nitrogen to approximately 30 barg and twice with carbon monoxide to approximately 25 barg and was then heated, by means of electrical heating coils, to a temperature of 190°C under 8 barg pressure of carbon monoxide. A rapid and consistent rate of stirring (1500 rpm) was employed. Once stable at temperature, the aqueous iridium catalyst solution was injected into the autoclave. Simultaneously, the autoclave was pressurised to 22 barg with carbon monoxide fed from the ballast vessel. The pressure in the autoclave was subsequently maintained at 22.0 barg with carbon monoxide fed from the ballast vessel. The partial pressure of carbon monoxide was calculated to be approximately 8 bar when the calculated methyl acetate concentration was 15 % by weight. The reaction temperature was maintained within  $\pm 1$  °C of the desired reaction temperature (190 °C).

Gas uptake from the ballast vessel was measured throughout the course of the experiment and used to calculate carbonylation rate. After uptake of carbon monoxide from the ballast vessel has ceased the autoclave was isolated from the gas supply and was cooled. The autoclave was vented and samples of the liquid reaction composition were analysed by gas chromatography. The major product in each batch carbonylation experiment according to the present invention was acetic acid. By-product yields are collated in Table 6.

Examples 15-21 and Experiments J-N

In Examples 15-17 additional methyl iodide (3 molar equivalents to tungsten) was added to compensate for probable loss of methyl iodide to tungsten iodocarbonyl components. Experiment M shows that simple addition of this extra methyl iodide to an un-promoted iridium reaction did not cause a significant increase in reaction rate.

The results given in Table 6 show that tungsten promotes iridium catalysed methanol carbonylation (compare Examples 15-17 with Experiments J-L).

Further Experiments

Further experiments (Experiment N and Examples 18-21) were performed using the same 300ml autoclave apparatus as for tungsten. Examples 18 to 20 show the effect of increasing the amount of zinc promoters and Example 21 shows the effect of cadmium promoter.

Table 5 Autoclave Charges

Experiment	Catalyst System (equivalents)	Catalyst $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (g)	Promoter	Amount of Promoter (g)	Methyl Acetate (g)	Water (g)	Methyl iodide (g)	Acetic Acid (g)	Other Amount(g)
Experiment J	Ir	0.552	-	-	48.01	16.97	8.99	75.58	
Experiment K	Ir	0.552	-	-	48.02	16.97	8.99	75.58	
Experiment L	Ir	0.552	-	-	48.04	16.97	8.87	75.57	
Experiment M	Ir	0.552	-	-	48.01	16.96	12.19	72.24	
Example 15	Ir:W (1:5)	0.552	$\text{W}(\text{CO})_6$	2.758	48.00	16.97	12.19	69.49	
Example 16	Ir:W (1:5)	0.557	$\text{W}(\text{CO})_6$	2.755	48.00	16.95	12.18	69.49	
Example 17	Ir:W (1:5)	0.552	$\text{W}(\text{CO})_6$	2.757	48.00	16.96	12.19	69.50	
Experiment N	Ir:Ru (1:2)	0.552	-	-	48.01	16.99	9.80	74.02	$\text{Ru}_3(\text{CO})_{12}$ 0.667
Example 18	Ir:Zn (1:2)	0.552	$\text{ZnI}_2$	0.993	48.02	16.94	8.86	74.57	
Example 19	Ir:Zn (1:5)	0.554	$\text{ZnI}_2$	2.495	48.00	16.94	8.86	73.07	
Example 20	Ir:Zn (1:10)	0.554	$\text{ZnI}_2$	4.980	48.01	16.98	8.88	70.59	
Example 21	Ir:Cd (1:2)	0.552	$\text{CdI}_2$	1.140	48.02	16.95	8.87	74.42	

Table 6 Rate, By-product and Stability Data

Experiment	Catalyst System (equivalents)	Rate at calculated 26, 15 and 6% wt% methyl acetate concentration (Mol/l/hr) <sup>a</sup>	By-products reaction composition at end of Experiment			Appearance of Reaction Composition at End of Experiment
			[Ethyl Iodide] (ppm)	[Ethyl Acetate] (ppm)	[Propionic Acid] (ppm)	
Experiment J	Ir	11.7 8.2 4.6	115	223	4	Orange solution
Experiment K	Ir	11.6 8.4 5.1	114	188	9	Orange solution
Experiment L	Ir	11.4 7.7 3.9	234	307	<2	Orange solution
Experiment M	Ir	11.4 8.6 4.2	100	179	<2	Orange solution
Example 15	Ir:W (1:5)	13.2 9.6 4.8	295	326	<2	Orange solution + blue solid
Example 16	Ir:W (1:5)	12.3 9.9 4.9	328	288	<2	Orange solution + blue solid
Example 17	Ir:W (1:5)	13.0 9.9 4.0	315	335	<2	Orange solution + blue solid
Experiment N	Ir:Ru(1:2)	20.6 15.6 9.0	405	253	19	Orange solution
Example 18	Ir:Zn(1:2)	14.5 10.9 6.5	400	410	18	Orange solution
Example 19	Ir:Zn(1:5)	15.6 12.8 8.1	408	408	10	Orange solution
Example 20	Ir:Zn(1:10)	15.8 13.6 9.3	439	394	18	Orange solution
Example 21	Ir:Cd(1:2)	13.5 12.5 9.5	-	-	-	Orange solution

a) Estimated rate error  $\pm$  10%

Water concentrations 9.7%, 7.0% and 4.6% respectively at 26, 15 and 6% methyl acetate;

methyl iodide about 5 to 8%, typically about 5 to 6% [eg in M initial methyl iodide is about 8%]

## Claims

1. A process for the carbonylation of an alkyl alcohol and/or a reactive derivative thereof which process comprises contacting in a carbonylation reactor said alcohol and/or a reactive derivative thereof with carbon monoxide in a liquid reaction composition comprising: (a) an iridium catalyst, (b) an alkyl halide, (c) at least a finite concentration of water, and (d) a promoter selected from the group consisting of cadmium, mercury, zinc, gallium, indium and tungsten.
2. A process as claimed in claim 1 in which the molar ratio of each promoter : iridium catalyst is (0.1 to 20) : 1, preferably (0.5 to 10) : 1.
3. A process as claimed in claim 1 or claim 2 in which a co-promoter selected from ruthenium, osmium and rhenium is present in the liquid reaction composition.
4. A process as claimed in claim 3 in which the molar ratio of each co-promoter : iridium catalyst is (0.1 to 20) : 1, preferably (0.5 to 10) : 1.
5. A process as claimed in any one of the preceding claims in which the concentration of water in the liquid reaction composition is in the range 1 to 15 % by weight, preferably 1 to 10 % by weight.
6. A process as claimed in any one of the preceding claims in which alkyl ester is present in the liquid reaction composition at a concentration in the range 1 to 70 % by weight, preferably 2 to 50 % by weight, more preferably 3 to 35 % by weight.
7. A process as claimed in any one of the preceding claims in which the concentration of alkyl halide in the liquid reaction composition is in the range 1 to 20 % by weight, preferably 2 to 16 % by weight.
8. A process as claimed in any one of the preceding claims in which the partial pressure of carbon monoxide in the reactor is in the range 1 to 70 bar, preferably 1 to 35 bar, more preferably in the range 1 to 15 bar.
9. A process as claimed in any one of the preceding claims in which the alkyl alcohol is methanol, the alkyl halide is methyl iodide and the product of the reaction comprises acetic acid and/or methyl acetate.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 96 30 2733

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.6)
D, Y	EP-A-0 643 034 (BP CHEM INT LTD) 15 March 1995 * the whole document *	1-9	C07C51/12
Y	US-A-4 358 411 (PORCELLI RICHARD V ET AL) 9 November 1982 * column 3, line 61 - column 4, line 49; example I *	1-9	
Y	FR-A-2 317 269 (METAUX PRECIEUX CIE) 4 February 1977 * the whole document *	1-9	
Y	US-A-4 096 164 (ELLGEN PAUL CLIFFORD ET AL) 20 June 1978 * the whole document *	1-9	
Y	GB-A-2 146 637 (DAICEL CHEM) 24 April 1985 * page 3, line 4 *	1-9	
Y	EP-A-0 031 606 (SHELL INT RESEARCH) 8 July 1981 * page 7, line 19 - line 28; claims 6,12; examples I-III, V-XIII *	1-9	<div>TECHNICAL FIELDS SEARCHED (Int. CL.6)</div> <div>C07C</div>
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 26 September 1996	Examiner Janus, S
<div>CATEGORY OF CITED DOCUMENTS</div> <div> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background U : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons &amp; : member of the same patent family, corresponding document</p> </div>			

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